Uncertainty Quantification in Geochemical Reactions

Daniel M. Tartakovsky*

Predictions of reactive transport in the subsurface are routinely compromised by both model (structural) and parametric uncertainties. We present a set of computational tools for quantifying these two types of uncertainty. The model uncertainty is resolved at the molecular scale where epistemic uncertainty incorporates aleatory uncertainty. The parametric uncertainty is resolved at both molecular and continuum (Darcy) scales. We use the proposed approach to quantify uncertainty in modeling the sorption of neptunium through a competitive ion exchange. This radionuclide is of major concern for various high-level waste storage projects due to its relatively long half-life, high solubility and low sorption properties. We demonstrate how parametric and model uncertainties affect one's ability to estimate the distribution coefficient. The uncertainty quantification tools yield complete probabilistic descriptions of key parameters affecting the fate and migration of neptunium in the subsurface, rather than the lower statistical moments. This is important, since these distributions are highly skewed.

We use such probabilistic parametrizations to derive a probability density function (pdf) formulation for advective transport of a solute that undergoes a heterogeneous chemical reaction involving an aqueous solution reacting with a solid phase. This system is described by a stochastic differential equation with multiplicative noise. We consider both linear and nonlinear kinetic rate laws, and derive effective kinetic rate constant for the mean field approximation describing the change in mean concentration with time. The effective rate constant decreases with increasing time eventually approaching zero as the system approaches equilibrium. This behavior suggests that a possible explanation for the observed discrepancy between laboratory measured rate constants on uniform grain sizes and field measurements may in part be caused by the heterogeneous distribution of grain sizes in natural systems.

*Department of Mechanical and Aerospace Engineering, University of California, San Diego, 9500 Gilman Drive, Mail Code 0411, La Jolla, CA 92093, USA. (dmt@ucsd.edu)